

Release of K, Cl, and S Species during Co-combustion of Coal and Straw

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Straw as a renewable energy source can either be used alone or be used in existing coal-fired power plants (co-combustion). The objective of the present work was to investigate the influence of fuel composition and interactions between various types of straw and coal on the release of K, Cl, and S species during co-combustion of coal and straw at temperatures between 800 and 1100 °C. The amount of HCl released during co-combustion was higher than expected on the basis of the combustion results of the pure fuels because of the reaction of the straw KCl with the coal silica. However, the amount of potassium released in gaseous form is only slightly lower than expected. The relative amount of sulfur released during co-combustion in comparison to the expected amount depends upon the temperature and the biomass share of the blends. At higher temperatures or lower straw share, the release is increased because of the reaction of the straw K₂SO₄ with the coal clay minerals. At lower temperatures and high straw share, available straw potassium and calcium capture some coal sulfur.

Introduction

An increased use of renewable energy sources for energy production is used to achieve the 8% reduction in CO₂ emissions of the European Union (EU) by 2012 (Kyoto objective). In this context, electricity from biomass and biomass-derived fuels is considered to be a possible energy source for the future. Straw and other high-alkaline (HIAL) biomasses are important fuel resources, and about 800 megatons of straw are actually usable for energy production in the EU and North America.¹

Straw as a renewable energy source can, for example, be used alone in grate-fired power plants. To increase the use of biomass, new biomass power plants have to be built. The initial capital investment is high. The firing of pure straw is characterized by high slagging and fouling propensity, high-temperature corrosion, limited steam temperatures, and relatively high emissions, e.g., HCl and SO₂.^{2–4}

Another option is to increase the use of straw in existing coal-fired power plants (co-combustion in PF or CFB boilers). The capital investments are much lower, and the advantage of the high efficiency of coal-fired power plants is taken. Besides the reduction of CO₂ emissions, the SO₂ emissions are reduced by co-combustion of coal with low-sulfur biofuels. Several co-combustion field tests have been conducted in Europe and North

America during the last few years.^{5–11} A final conclusion on these tests is thus that co-combustion of coal and straw is practically manageable for up to 20% straw share on energy basis. The corrosion rate and deposit formation are below those from 100% straw firing and closer to those in coal-fired power plants.

Recent laboratory investigations have shown that the release of K, Cl, and S species during combustion of pure straw is related to the chemistry of the combustion process.^{12–14} High amounts of potassium lower the SO₂ release by the formation of potassium sulfate. Silica decreases the release of potassium and promotes the release of SO₂ by potassium capture, inhibiting

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Table 1. Analysis of the Fuels Used in the HPMS Experiments

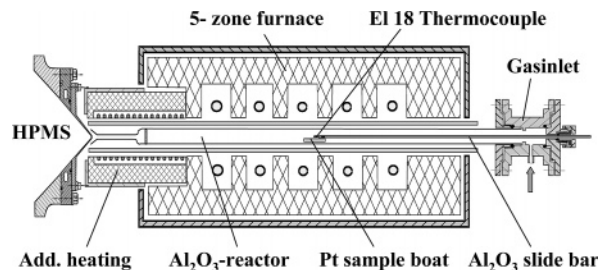
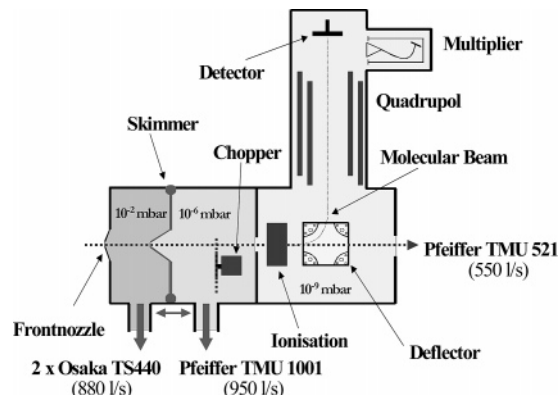
	HIAL2 oats	HIAL5 barley	HIAL7 carinata	HIAL10 wheat	Cocerr coal
moisture (%)	17.2	13.6	10.6	15.9	4.2
ash (% dry)	3.9	7.2	5.1	6.8	12.1
C (% dry)	48	45	45	46	70
H (% dry)	6.3	6.0	6.0	6.1	4.4
N (% dry)	0.93	0.76	1.1	0.59	1.29
S (% dry)	0.16	0.19	0.28	0.15	0.52
Cl (% dry)	0.06	1.10	0.06	0.30	0.03
Si (% dry)	0.29	0.82	0.06	1.50	3.58
Al (% dry)	0.006	0.008	0.008	0.04	1.29
Fe (% dry)	0.006	0.005	0.007	0.02	0.61
Ca (% dry)	0.80	0.39	0.74	0.34	0.10
Mg (% dry)	0.08	0.10	0.07	0.07	0.07
Na (% dry)	0.14	0.30	0.01	0.02	0.06
K (% dry)	0.61	2.50	1.70	1.30	0.21
P (% dry)	0.10	0.05	0.17	0.08	0.01
LHV dry (MJ/kg)	17.4	16.5	16.7	16.8	26.0
K/S (MJ/kg)	3.8	13.2	6.1	8.7	0.4
K/Si (MJ/kg)	2.1	3.1	28.3	0.9	0.1
S/Cl (MJ/kg)	2.7	0.2	4.7	0.5	35.1
K/Cl (MJ/kg)	10.2	2.3	28.3	4.3	7.0

the sulfate formation. The release of potassium depends upon the content of chlorine in the fuels rather than on the potassium content. The kind of binding (organic or inorganic) of the elements, e.g., sulfur, has a strong influence on the release, too. More volatile species are less influenced by the ash composition than less volatile species. Thermodynamic calculations and laboratory experiments reveal that similar mechanisms as mentioned above are relevant in co-combustion of biomass and coal.^{15–17} Because different types of straw and especially straw and coal have completely different fuel properties and ash compositions, different effects can be dominant depending upon the mixture.

The objective of the present work was to investigate the influence of fuel composition and interactions between various types of straw and coal on the release of K, Cl, and S species during co-combustion of coal and straw at temperatures between 800 and 1100 °C. For this reason, laboratory combustion experiments have been carried out for coal, four types of straw, and several coal/straw blends with different biomass share. The combustion products were investigated online by high-pressure mass spectrometry (HPMS). Crystalline compounds of the ashes were identified by X-ray powder diffraction (XRD).

Experimental Section

Fuel Preparation. Samples of four Danish and Spanish types of straw and one Columbian coal “Cocerr” were collected and prepared for analysis. The coal was dried in air at a temperature of 105 °C for 20 h, and visible stones were removed. The biomass fuels were air-dried at room temperature and archived up to the time of the study under dry conditions. All fuels were milled through a 1 mm screen for the present studies. The chemical analysis for the investigated fuels is presented in Table 1. The presented biomasses were chosen because of their different ratios of K/Si, K/Cl, and K/S, which are predicted to have a major influence on the release of inorganic species. The following coal/straw blends were prepared on the basis of the heating values (LHV dry) of the

**Figure 1.** Setup used for the combustion experiments.**Figure 2.** Schematic of the HPMS system.

fuels: 80% coal and 20% straw (sample names: 20% HIAL_n) and 50% coal and 50% straw (sample names: 50% HIAL_n).

Experimental Setup. Hot-gas analysis in this study was conducted using HPMS. HPMS has been proven to be a reliable method for studying high-temperature, ambient pressure environments established in the present studies.^{17–19} For all measurements in this study, the HPMS system has been coupled to a high-temperature reactor. Figure 1 shows the reactor setup used for the combustion experiments. A detailed description of the system used in this study is given by Wolf.²⁰

A platinum sample boat containing 50 mg of coal and/or straw material was attached to the end of a 6 mm diameter alumina rod. The rod was inserted into a 21 mm inner diameter tubular alumina reactor that was housed in a high-temperature furnace. The furnace was maintained at a constant temperature of either 800 or 1100 °C in the combustion zone. However, during combustion, the temperature possibly increased above the furnace temperature. A gas mixture of 20% O₂ in helium flowed through the reactor at a flow rate of 3.0 sl/m (standard liters per minute). Therefore, the residence time of combustion products in the reactor before sampling was in the range of 0.15–0.3 s, depending upon the furnace temperature.

The end of the alumina reactor was coupled to the sampling orifice of the HPMS device, to sample the high-temperature combustion products. The orifice protruded into the furnace to maintain an elevated temperature to prevent condensation of gas-phase species on the tip of the orifice. The furnace provided an extra heating zone near the exit of the furnace, to prevent combustion products from condensing on the reactor tube walls.

Figure 2 shows a schematic of the HPMS system used for the experiments in this study. The HPMS consists of three differentially pumped vacuum chambers. Gases entering the 300 μm orifice undergo a supersonic free jet expansion into the first chamber, and

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intermolecular collisions between molecules are decreased drastically ~ 10 orifice diameters downstream from the orifice. At that point, the expansion has attained free molecular flow. The condensation of the gas-phase species is inhibited, and intermolecular reactions are quenched. Therefore, high-temperature combustion products can be sampled directly, without being altered on their way to the HPMS detector. After the sampled gases are collimated by a conical skimmer with a diameter of 1 mm, they form a molecular beam that is directed into the third stage of the vacuum system. In this stage, ions are formed by electron impact ionization with a nominal electron energy of 30 eV. After the ions passed a deflector system, they are filtered in a quadrupole mass analyzer and detected by an off-axis electron multiplier with a conversion dynode applied. A complete computer and software package was used to control all mass scanning parameters and for collecting the preamplified multiplier signal, as a function of time and mass/charge (m/z) ratio.

At the beginning of each experiment, the platinum sample boat was held in the cooled zone of the reactor at ~ 30 °C and a background spectrum was acquired for ~ 30 s. While the HPMS was kept in a constantly scanning mode, the sample boat was inserted into the heated region of the reactor and the combustion process was monitored over time. The species sampled were O_2^+ , CO^+ , CO_2^+ , Na^+ , NaCl^+ , K^+ , KCl^+ , SO_2^+ , and HCl^+ . For the quantification of the release of the sampled species, the ion signals were integrated over time. The duration of the entire combustion process, including ash cooking, was dependent upon the furnace temperature and the fuel type. A total of 2 min was the required maximum. A total of 10 identical samples were measured, and the results were averaged to ensure reproducibility. During one series of measurements, all settings were kept constant, to ensure comparability.

Results and Discussion

The HPMS results for the pure fuels and the blends were similar to former results for pure biomass.¹⁹ Two phases of combustion could be observed for all samples: devolatilization and char combustion. The char combustion phase for coal and for the blends was generally longer than the char combustion phase for pure straw. The release of inorganic species during char combustion at 800 °C was generally lower than during char combustion at 1100 °C.

The gas/solid interaction times in the alumina-tube flow reactor used in the experiments and the batch nature of the HPMS sampling, with rapid quenching of the high-temperature products, are very short (0.15–0.3 s). Therefore, mainly fast gas/solid reactions and reactions occurring during char combustion are relevant for the obtained results. The gas/solid interaction times are considerably longer in fluidized bed combustion than in pulverized fuel boilers. Therefore, the HPMS experiments rather represent the combustion behavior in pulverized fuel boilers. However, possible gas/solid interactions or condensation of gas-phase species in colder regions of the pulverized fuel combustor are not represented. For example, the reactions of alkali species with clay minerals, discussed later, probably take place to a much higher degree in the combustion chamber of a power plant than in the presented flow reactor experiments. However, these reactions are likely very reactor-specific.

Combustion of Coal/Straw Blends at 1100 °C. In a first step, the four pure straw samples, the pure coal, and the biomass/coal blends were combusted in He/20% O_2 at 1100 °C. The integrated intensities of HCl^+ , K^+ , KCl^+ , and SO_2^+ are shown in Figure 3. The identified crystalline compounds of the ashes are presented in Figure 4.

A comparison of Figure 3 and Table 1 reveals that, similar to former investigations,¹⁹ the amount of SO_2 , K, and Cl species

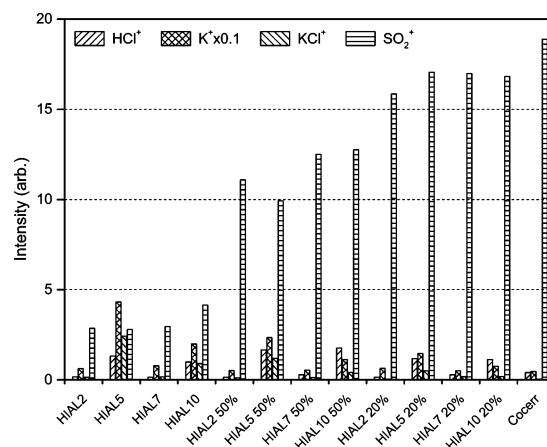


Figure 3. Measured intensities of species released during combustion of straw, coal, and coal/straw blends at 1100 °C in He/20% O_2 .

	Fe_2O_3	CaO	$\text{Al}_2\text{Si}_2\text{O}_7$	SiO_2	$\text{Ca}_2\text{Al}_2\text{Si}_2\text{O}_8$	KAlSi_3O_8	(K,Ca)silicate	K_2SO_4	$\text{K}_2\text{Na}(\text{SO}_4)_2$	KCl	amorphous
HIAL2											
HIAL2 50%											
HIAL2 20%											
Cocerr											
HIAL5											
HIAL5 50%											
HIAL5 20%											
Cocerr											
HIAL7											
HIAL7 50%											
HIAL7 20%											
Cocerr											
HIAL10											
HIAL10 50%											
HIAL10 20%											
Cocerr											

Figure 4. Crystalline compounds of the 1100 °C ashes identified by XRD. Black shading, main phase; gray shading, minor phase.

released during the combustion experiments of the pure samples does not correspond to the amount of the corresponding elements found in the analysis. For example, the coal contains almost 0.5% sulfur, 1.9–3.5 times more than the straw samples. Not surprisingly, the largest amount of SO_2 was released during combustion of coal. However, the released amount of SO_2 during combustion of coal was 4.5–6.7 times higher than during combustion of straw. Some reasons can be found in the XRD analysis of the ashes. A high amount of potassium in the straw samples in comparison to the coal leads to a retention of sulfur via the formation of K_2SO_4 , reducing the SO_2 emission. The silica in the coal and in HIAL10 to a minor extent binds potassium by the formation of amorphous silicates. Thus, less or no potassium is free for K_2SO_4 formation. Therefore, the SO_2 release is higher for HIAL10 and much higher for coal than for the other straw samples. The release of KCl and HCl is mainly influenced by the amount of chlorine in the initial samples. However, some straw ashes contain a certain amount of KCl . The chlorine is in contrast to previous investigations¹² not exclusively released. Therefore, these samples show a lower release of Cl species than expected from the chemical analysis. For example, HIAL5 has a 3.7 times higher chlorine content than HIAL10. Because of solid KCl remaining in the ash of

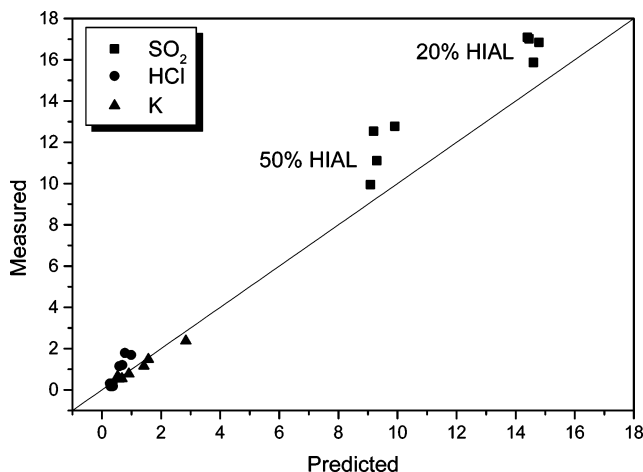
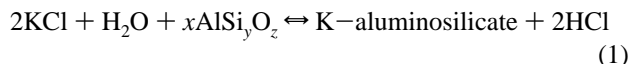


Figure 5. Parity diagram depicting the measured versus predicted amounts of SO_2 , HCl , and K released during co-combustion at 1100°C in $\text{He}/20\% \text{O}_2$.

HIAL5, the release of gaseous KCl is only 2.6 times higher and that of HCl is only 1.4 times higher. Similar to K_2SO_4 , the formation of KCl is inhibited by silica. The K^+ signals measured by HPMS are mostly fragment ions from KCl^+ and partly from KOH^+ and K_2SO_4^+ , which are the main alkali-containing species. Alkali species released as free metals are not likely to contribute to these intensities.¹⁸

The origin of the changes in the emissions observed for the coal/straw blends in comparison to the pure fuels cannot be easily determined from Figure 3. Therefore, the parity diagram in Figure 5 displays the predicted versus measured amounts of SO_2^+ , HCl^+ , and K^+ for all coal/straw blends. Thus, it is possible to draw conclusions, whether the observed changes were caused by dilution of a certain element in the fuel blend or whether any chemical interactions occurred. The predicted values were based on a linear combination of the measured values for the pure fuels.

The points representing the measured and predicted amounts of HCl and K lie close to the diagonal parity line, indicating that there were no or only weak interactions between the pure fuels in the blend that effect the release of Cl and K species. In the ashes of the blends, no chlorine-containing phases are present, in contrast to the straw ashes. Potassium is captured by clay minerals of the coal according to reaction 1



resulting in a slightly increased release of HCl . The strongest effect is observed for HIAL5/coal blends. HIAL5 has the highest content of both, chlorine and potassium, besides a medium content of sulfur and silica, resulting in the formation of the highest amount of KCl , which reacts with the silicates of the coal during co-combustion. The adsorption of potassium by silicates seems to have only a very weak effect on the release of potassium. The amount of potassium released during co-combustion is only slightly lower than expected on the basis of the combustion results for the pure fuels.

During combustion of all blends, more SO_2 was detected than expected on the basis of the combustion results of the pure fuels. The reason can be found in the XRD analysis of the ashes. In the ashes of the pure straw samples, the sulfur is partly bound as K_2SO_4 . During co-combustion, the potassium is captured by clay minerals of the coal, resulting in the formation of KAlSi_xO_y and an increased release of sulfur. The time versus intensity

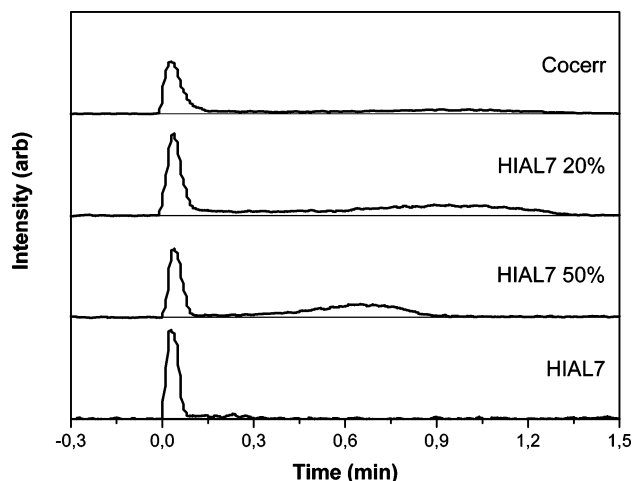


Figure 6. Intensity versus time profiles of SO_2 released during combustion of HIAL7, coal, and HIAL7/coal blends at 1100°C in $\text{He}/20\% \text{O}_2$.

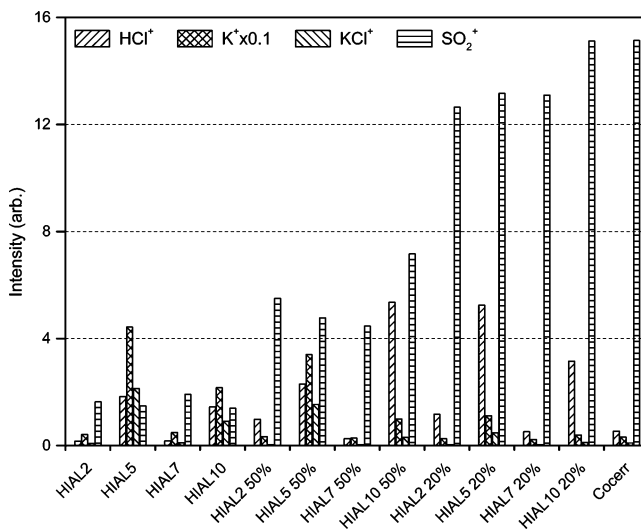


Figure 7. Measured intensities of species released during combustion of straw, coal, and coal/straw blends at 800°C in $\text{He}/20\% \text{O}_2$.

profiles of SO_2 shown in Figure 6, considering HIAL7/coal blends as an example, confirm this. The release of volatile, likely organic-bound sulfur is only slightly influenced by interactions between the fuels. Because of the reaction of K_2SO_4 with clay minerals of the coal, which is relatively slow and occurs at high temperatures, the release of sulfur is increased during char combustion of the blends. This is in good agreement with measurements on the influence of additives on the sulfur release during combustion of straw.¹⁹ The investigated additives mainly influenced the less volatile sulfur, which is released during char combustion.

Combustion of Coal/Straw Blends at 800°C . In a second step, the four pure straw samples, the pure coal, and the coal/straw blends were combusted in $\text{He}/20\% \text{O}_2$ at 800°C to investigate the influence of the combustion temperature. The integrated intensities of HCl^+ , K^+ , KCl^+ , and SO_2^+ are shown in Figure 7. The parity diagram in Figure 8 displays the predicted versus measured amounts of SO_2^+ , HCl^+ , and K^+ for all coal/straw blends. The identified crystalline compounds of the ashes are presented in Figure 9.

In comparison to 1100°C , the release of SO_2 is decreased, mainly because of the decrease of SO_2 release during char combustion. Similar to the results of the measurements at 1100°C , the release of SO_2 is strongly influenced by the formation

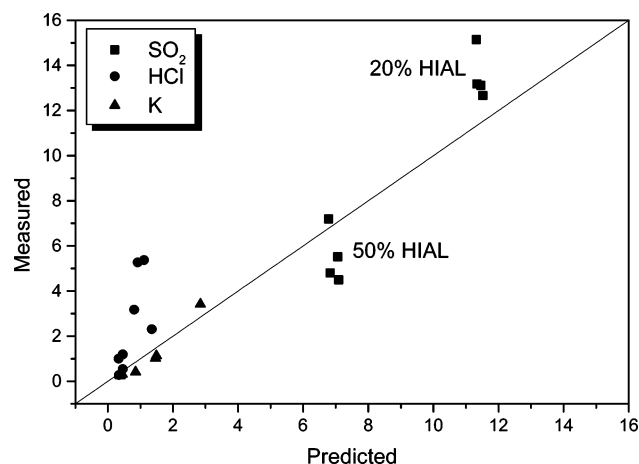


Figure 8. Parity diagram depicting the measured versus predicted amounts of SO_2 , HCl , and K released during co-combustion at 800°C in $\text{He}/20\% \text{O}_2$.

	Fe_2O_3	CaO	SiO_2	$\text{Ca}_2\text{Al}_2\text{SiO}_4$	KAlSiO_4	CaSO_4	$\text{K}_2\text{Ca}(\text{SO}_4)_2$	K_2SO_4	$\text{K}_3\text{Na}(\text{SO}_4)_2$	KCl	KCaPO_4
HIAL2											
HIAL2 50%											
HIAL2 20%											
Cocerr											
HIAL5											
HIAL5 50%											
HIAL5 20%											
Cocerr											
HIAL7											
HIAL7 50%											
HIAL7 20%											
Cocerr											
HIAL10											
HIAL10 50%											
HIAL10 20%											
Cocerr											

Figure 9. Crystalline compounds of the 800°C ashes identified by XRD. Black shading, main phase; gray shading, minor phase.

of sulfates. The release of KCl and HCl from the pure samples as well as from the blends is in the same order of magnitude as at 1100°C .

It can be seen from the parity diagram in Figure 8 that there is a much higher increase of HCl release during co-combustion at 800°C than at 1100°C . In the 800°C ashes of the pure straw samples, KCl is a main phase, while in the 1100°C ashes of the pure straw samples, KCl is a minor phase. Similar to the 1100°C ashes of the blends, no chlorine-containing phases are present in the 800°C ashes of the blends, other than 50% HIAL5. Thus, more KCl is available for the reaction with SiO_2 according to reaction 1, resulting in the observed high release of HCl . Similar to the results of the 1100°C experiments, the strongest effect is observed for HIAL5/coal blends. The influence of interactions on the release of potassium is slightly stronger than at 1100°C .

The interactions between straw and coal during co-combustion lead to different effects on the release of SO_2 . During combustion of blends with 20% straw, more SO_2 was detected than expected on the basis of the combustion results of the pure fuels, whereas during combustion of blends with 50% straw, less SO_2 was detected, other than in the case of HIAL10. The reason

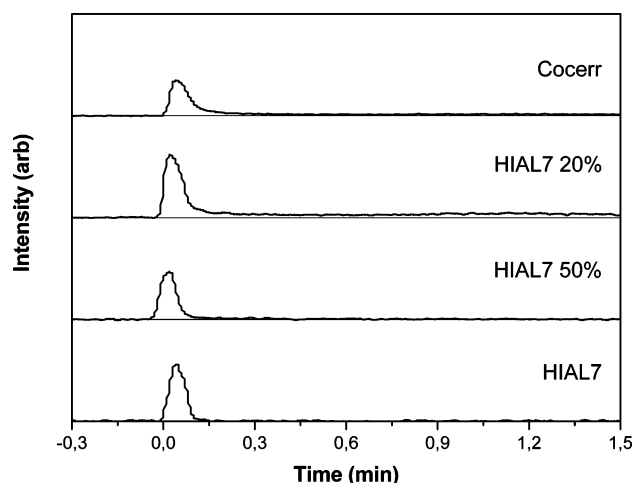


Figure 10. Intensity versus time profiles of SO_2 released during combustion of HIAL7, coal, and HIAL7/coal blends at 800°C in $\text{He}/20\% \text{O}_2$.

can be found in the XRD analysis of the ashes (Figure 9) and the time versus intensity profiles of SO_2 shown in Figure 10, considering HIAL7/coal blends as an example.

During combustion of coal/straw blends with 50% straw, the formation of stable sulfates is dominant, decreasing the overall SO_2 release. Besides CaSO_4 , which is the stable sulfate in the coal ashes, different alkali sulfates are stable in the ashes of the blends with 50% straw. In the case of 50% HIAL2, CaSO_4 becomes a main crystalline phase. It appears, from Figure 10, that the release of volatile sulfur is lower than expected on the basis of the combustion results of the pure fuels. No sulfur is released during char combustion.

During combustion of coal/straw blends with 20% straw, the reaction of sulfates with silica is dominant, resulting in an increased SO_2 release. CaSO_4 , as a minor crystalline phase, is the only stable sulfur-containing phase in the ashes of these blends. Because of the reaction of the alkali sulfates with the silica of the coal, a notable amount of sulfur is released during the char combustion phase.

Conclusions

In this work, laboratory combustion experiments with coal, four types of straw, and several coal/straw blends with different biomass share have been performed in the temperature range of 800 – 1100°C under oxidizing conditions to examine the interactions of the fuels during co-combustion. Hot-gas analysis was performed, via HPMS.

Measurements of the pure fuels show that the release of inorganic constituents such as potassium and sulfur from the fuel during combustion is strongly dependent upon other inorganic constituents, such as silicon and chlorine, and the type of binding (inorganic or organic).

At 1100°C , the amount of KCl and HCl released during co-combustion correlates well with the ratio of fuels. The release of HCl is slightly increased for blends with straw, having high contents of both, potassium and chlorine, because of the reaction of the straw KCl with the coal silica. Because of the reaction of the straw K_2SO_4 with the coal silica, the release of SO_2 is higher during co-combustion than expected on the basis of the combustion results of the pure fuels.

At 800°C , only the amount of KCl released during co-combustion correlates well with the ratio of fuels. The release of HCl is increased during co-combustion. There is a higher increase in HCl release at 800°C than at 1100°C because more

KCl is available from the straw. In the case of 20% straw, the amount of SO₂ released during co-combustion is higher than expected on the basis of the combustion results of the pure fuels because of the reaction of the straw K₂SO₄ with the coal silica. In the case of 50% straw, the release of SO₂ is lower because of the capture of sulfur by available straw potassium and calcium.

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